

The Ozone Weekend Effect in California: Evidence Supporting NO_x Emission Reductions

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ABSTRACT

Ozone is typically higher on weekends than on weekdays at many of California's air-monitoring stations. This "ozone weekend effect" occurs despite substantially lower weekend emissions estimates for the major ozone precursors – ROG and NO_x. Because weekend NO_x emissions decrease more (proportionally) than ROG, some conclude that NO_x emission reductions would undermine ozone attainment efforts. However, the evidence permits the contrary conclusion, that NO_x emission reductions would expedite attainment of ozone standards. In this regard, several observations are important. (1) After thirty years in which ROG emissions declined faster than NO_x emissions, weekends have higher ozone than weekdays; weekends have been left behind. (2) At peak ozone sites, the weekend effect is usually relatively small. (3) The weekend effect decreases when ozone-forming potential is high. (4) Ozone generation aloft (100 to 1500 meters above the surface) appears to be NO_x-limited and carryover aloft may strongly affect surface ozone, especially under episode conditions. And, (5) simulation models have not yet demonstrated the ability to generate enough ozone aloft to fully incorporate the effects of carryover aloft. These observations clearly show it is premature (at least) to conclude that the ozone weekend effect invalidates NO_x emission reductions included in ozone attainment plans.

IMPLICATIONS

Fully informed policy-makers make the best decisions. At this time, public discussion of the "ozone weekend effect" has mostly reflected the viewpoint that weekend NO_x reductions mimic regulatory NO_x reductions, which are thereby shown to be counter-productive as an ozone abatement strategy. An alternative interpretation of the evidence is presented here to help policy-makers consider the efficacy of NO_x reductions in the absence of a validated explanation of the weekend effect. Presently available data and analyses are inconclusive. New field studies, selected laboratory experiments, and improved models will be needed to resolve the central issues.

INTRODUCTION

Ozone concentrations are typically higher on weekends compared to weekdays in many parts of California.¹ This phenomenon, referred to here as the "ozone weekend effect," occurs despite substantially lower weekend emissions estimates for the main ozone precursors – reactive organic gases (ROG) and oxides of nitrogen (NO_x). Although the ozone weekend effect has been studied for more than twenty years,^{2,3,4} a validated explanation for it is not yet available.

The issue is controversial because the ozone weekend effect is viewed by some as proof that NO_x-reducing regulations are unwise because they would undermine the progress that ROG reductions alone would otherwise achieve. If this view is correct, so-called “NO_x disbenefits” will delay or even prevent attainment of ozone air quality standards.

This paper presents an alternative explanation of field observations and model results. According to this explanation of the evidence, NO_x reductions not only would not jeopardize ozone attainment goals but would further these goals expeditiously.

ANALYSES CONCERNING THE OZONE WEEKEND EFFECT

To understand the ozone weekend effect and its implications, the following questions must be answered:

1. When ozone molecules are detected at a surface monitor, where, when, and under what conditions were they generated?
2. On weekdays versus weekends, do ozone molecules detected at surface monitors represent different places, times, and conditions in different proportions?
3. How do the answers to these questions relate to regulatory reductions of ROG and NO_x emissions?

The following sections consider these three questions in relation to various analyses used to investigate the ozone weekend effect and its relationship to potential effects of regulatory NO_x reductions.

Ozone and Emission Trends

In California, historical changes in ozone in response to ROG and NO_x reductions lead to an inescapable conclusion: while ROG emissions decreased faster than NO_x emissions, ozone decreased faster on weekdays than on weekends. Ozone decreased strongly on both weekdays and weekends, but comparatively, weekends were “left behind.” Two analyses illustrate the patterns that lead to this conclusion.

First, ozone trends were compared for weekdays and weekends from 1980 to 1998 in the South Coast Air Basin (SoCAB).⁵ For each year, daily maximum ozone measurements were summarized by day-of-week. For each day of the week, the day with the highest ozone measurement was discarded and the ten highest remaining values were averaged. Trends in the average weekday results were compared to trends in the average weekend results.

Table 1 presents emissions inventories⁶ of ROG and NO_x for 1980 and 2000 in four areas of California, including the SoCAB, where the rate of ROG reductions has been about 1.5 times the rate of NO_x reductions. Table 2 shows the percent decrease in ozone on weekdays and weekends over this period for five sub-regions of the basin. In all five sub-regions, ozone on weekdays improved significantly more than it did on weekends.

Figure 1 shows the weekday and weekend trends for ozone at five sites in the SoCAB. Arranged from west to east, the sites are Los Angeles, Azusa, Upland, Riverside, and Crestline (Lake Gregory); the figure clearly illustrates how weekend ozone has improved more slowly than weekday ozone, and that weekend ozone now surpasses weekday ozone. Today, the highest ozone concentrations in the South Coast Air Basin (SoCAB) typically occur on weekends, especially on Sunday, rather than on weekdays. Sundays also tend to record the highest ozone concentrations in the San Francisco Bay Area Air Basin (SFBAAB), the San Joaquin Valley Air Basin (SJVAB), and the Sacramento Metropolitan Area (SMA), though the differences with respect to weekdays are much less pronounced in the latter two regions (see Table 3).

Second, Tran and Austin¹ prepared a rigorous assessment of the ozone weekend effect in the SoCAB, the SFBAAB, and the SMA. The methods they applied included appropriate filters to remove long-term and seasonal trends, an explicit accounting for serial dependency, and robust estimation of means to limit the impact of outliers. Their work considered the ozone weekend effect before and after the introduction of California's Phase 2 reformulated gasoline (RFG2), which occurred in 1996. According to emissions inventories, RFG2 reduced total ROG emissions about 50% more than it reduced NO_x emissions.⁷ Although RFG2 has been credited with reducing ambient ozone generally,⁷ the gap between weekdays and weekends widened significantly immediately following its introduction. In addition, Sunday emerged as the day-of-week with the highest ozone concentrations in all three areas considered by Tran and Austin.¹

Since an emphasis on ROG reductions has left weekends behind, some obvious questions arise. Are greater NO_x reductions needed to reduce the highest ozone concentrations in California, which now occur on weekends, on Sundays in particular? When ozone molecules are measured at the surface on Sundays, where did they come from, under what conditions were they formed, and in what proportions? These thoughts are explored further in connection with the current spatial distribution of the ozone weekend effect in California.

Spatial Distribution of the Ozone Weekend Effect

In California air basins, the ozone weekend effect is relatively small in the areas that determine attainment status. These are the most relevant areas when considering possible NO_x "disbenefits" with respect to attainment goals.

Previous research quantified the ozone weekend effect at monitoring sites in four major areas of California. In addition to the three air basins considered by Tran and Austin,¹ the staff of the California Air Resources Board (CARB) quantified the ozone weekend effect in the San Joaquin Valley Air Basin.⁸ As shown in Table 3, the ozone weekend effect in all four regions is significantly greater (proportionally) in the urbanized areas than in the suburban and rural areas downwind. Table 4 identifies the monitoring locations (by AIRS identification number) that were considered in each category. The suburban and rural areas that exhibit smaller weekend effects are the same areas that record the highest

ozone concentrations in each region. In other words, smaller weekend effects usually occur in those areas that determine a region's attainment status. In these areas, the ozone weekend effect is about 20% in the South Coast and San Francisco Bay Area Air Basins and 5% in California's interior valleys.

This spatial pattern in the ozone weekend effect may occur for at least two reasons that are not mutually exclusive; both may play a role in determining the overall weekend effect. The first reason relates to classic results in photochemistry in which ozone formation in areas near emission sources tends to be ROG-limited while ozone formation moves from ROG-limited to NO_x-limited as the distance downwind from emission sources increases. Those who view the weekend effect as a demonstration of "disbenefits" due to lower NO_x and higher ROG/NO_x ratios on weekends discuss this viewpoint in detail.

The second reason for the spatial pattern in the ozone weekend effect relates to a major phenomenon in ozone photochemistry, titration or "scavenging" of ozone molecules and radicals by nitric oxide (NO). The role that scavenging appears to play in the ozone weekend effect is discussed at some length in the next section.

Ozone/Radical Scavenging and the Ozone Weekend Effect

Nitric oxide is the primary species in fresh NO_x emissions, typically 90% or more.⁸ The NO emissions scavenge ozone and radicals according to two fast reactions in the atmosphere. Ozone combines with NO to produce O₂ and NO₂, and organic radicals (RO• or ROO•) combine with NO to yield R• or RO• and NO₂. The prevalence of these reactions appears to play a significant role in the ozone weekend effect.

Emissions of NO at the surface in urbanized areas are relatively abundant on weekdays but relatively scarce on weekends, particularly on Sundays. Fresh NO emissions at ground level quickly scavenge ozone molecules and reduce the ozone concentrations measured by surface monitors. This scavenging phenomenon is much greater on weekdays than on weekends. Four observations are given to support this claim.

Day-of-week profiles for traffic and NO_x. As part of a larger investigation of the ozone weekend effect, we analyzed patterns in traffic data and compared them to patterns in air quality data. These analyses were limited to the SoCAB, but they yielded significant results that may represent other urbanized areas.^{9,10}

Motor vehicle activity differs dramatically between weekdays and weekends, especially Sundays. The largest discrepancy between weekdays and weekends is between 6:00 a.m. and 11:00 a.m., with a lesser but possibly important differences between 3 p.m. and 7 p.m. Figure 2 shows day-of-week composite profiles for hourly volumes of light-duty vehicles at 15 Weigh-in-Motion (WIM) stations in the SoCAB. Figure 3 shows these patterns for heavy-duty vehicles for the same stations. The figures are based on data archived by the California Department of Transportation throughout the year 2000. These figures are similar to those in the work cited but represent a full year of more recent data.

Figure 4 shows composite profiles for day-of-week NO_x measurements at eleven air quality monitors in Los Angeles and Orange Counties, many of them near the WIM stations used to characterize traffic patterns. The profiles for traffic and for NO_x are consistent with emission inventory data¹¹ for the year 2000 that indicate over 60% of NO_x emissions in the SoCAB are produced by on-road motor vehicles. When all mobile sources are considered, they account for almost 90% of the NO_x emissions in the SoCAB. Source tests show that NO_x emissions are predominantly in the form of NO, which is converted to NO_2 and other nitrogen-containing species in the atmosphere.⁸

From the air quality and emissions inventory data, it is clear that fresh NO emissions are much greater on weekdays than on weekends, especially on Sundays. The opportunity for fresh NO to scavenge ozone near the surface is clearly much greater on weekdays than on weekends.

Vertical profiles for NO_x and ozone. Vertical profiles for NO_x and ozone are not commonly available apart from intensive field studies. Major field studies of ozone in Southern California were conducted in 1987 and 1997. Both studies included some vertical profiles of ozone and/or NO_x measured by aircraft, ozonesondes, or lidar. The studies, however, were not designed with the weekend effect in mind. In fact, the 1987 study sought representative weekday episodes, while the 1997 study sought representative weekend episodes. Ambient ozone concentrations and emissions of ozone precursors both declined dramatically in the ten years between these studies. As a result, weekdays and weekends between and within the studies are not easily compared with confidence.

An analysis of the ozonesonde data from the 1997 South Coast Ozone Study suggests that afternoon differences between ozone at the surface and at 100 meters are greater on weekdays than on weekends. For this analysis, we estimated the ozone concentration at 100 meters by interpolating between the nearest values below and above 100 meters. For each day, the measurements closest to the surface after equilibration were used to estimate the surface concentration. Because a measure of subjective judgement was required in this analysis, we took care to err toward equal ozone values at the surface and aloft. The results, shown in Table 6, may indicate that ozone on weekdays is prevented from mixing down to ground level where surface monitors can measure it. If so, the prime suspect is an extra measure of scavenging by fresh NO emissions near the surface on weekdays that does not occur on weekends.

Different weekend effects at two nearby locations. The highest ozone concentrations in the SFBAAB are typically measured at Livermore. Recently the Livermore monitor was moved a short distance. The move was precipitated by analyses showing that NO emissions from a newly activated bus terminal a short distance upwind of the old location were scavenging ozone and depressing the measured ozone concentrations. Like most public transit systems, activity at the bus terminal was much lower on weekends than on weekdays. Route schedules from the Livermore Amador Valley Transit Authority show greatly reduced service on Saturdays and no service on Sundays. At the old monitoring

location, daily maximum ozone concentrations on Sundays were about 32 percent higher compared to Fridays. At the new monitoring location, emissions from the bus terminal have little effect and daily maximum ozone on Sundays is only 23 percent higher compared to Fridays. Ozone on Sundays did not decrease; rather, ozone on Fridays increased. This analysis shows that at a significant portion of the ozone weekend effect can be due to day-of-week differences in ozone scavenging at the surface by fresh NO emissions. It is possible that much of the remaining 23 percent difference between Sundays and Fridays at the new Livermore location is due to ground level suppression of ozone due to scavenging by NO emissions from sources that are plentiful on weekdays but relatively scarce on weekends.

Comparison of total oxidant on weekdays and weekends. If surface emissions of NO depress surface ozone concentrations through scavenging, the weekend effect for the sum of ozone and NO₂ (total oxidant) should be smaller than the ozone weekend effect. Table 7 summarizes the weekend effect for total oxidant in the SoCAB based on the ozone seasons (May through October) for 1998 through 2000. For all locations, the largest weekend effect for total oxidant was 8.7 percent and the basinwide average was 4.5%. These are drastically smaller than the values for the ozone weekend effect.

If differences in ozone scavenging at the surface on weekdays versus weekends is an important contributor to the ozone weekend effect, could there be circumstances in which ozone is so abundant that the scavenging of ozone by NO emissions on weekdays makes less of a difference? The next section considers this question.

Ozone-Forming Potential and the Ozone Weekend Effect

We evaluated the ozone weekend effect in the SoCAB under varying levels of ozone-forming potential (OFP).¹² The measured ozone levels were not used to characterize OFP because it would have introduced a sample-selection bias. For example, if high ozone on Fridays were the basis for selection, the weekend effect would be greatly underestimated because the highest Fridays would not necessarily be paired with the highest Sundays. Selection of Sundays with high ozone would bias the estimation the other direction. Other methods, such as using the weekly average will reduce but not remove selection biases. To minimize selection biases, a method of characterizing OFP based only on meteorology without regard to the measured ozone was used.

An equation developed by Larsen⁶ in a study of ozone-reducing benefits of reformulated gasoline was used to characterize daily OFP. The equation relates maximum ozone in the SoCAB each day to same-day meteorological measurements that relate to atmospheric dispersion and solar intensity. When values for these meteorological parameters are entered into the equation, they approximate daily OFP as it occurred in the years used to calibrate the equation (1993 and 1994). Measured ozone concentrations have since decreased, but the OFP values from the equation can still be used to indicate relative OFP today.

Using the OFP equation, days between mid-May and mid-October for six years (1992-1994 and 1996-1998) were assigned to three groups. Low OFP was defined as up to 0.12 ppm, medium was between 0.12 and 0.16 ppm, and high was greater than 0.16 ppm. The resulting groups were approximately equal in size, about 300 days each. Day-of-week differences in ozone were evaluated for each group. Days with low OFP are least relevant to the issues surrounding the ozone weekend effect, so emphasis is placed here on differences between the medium and high OFP groups.

For the medium OFP group, the ozone weekend effect was approximately 13 to 15%. This corresponds well with the weekend effect noted for high sites on all days from May through October. Under high OFP conditions, however, the ozone weekend effect was approximately 7 to 8%. That is, when the meteorological conditions are most relevant to attainment goals, ozone concentrations on weekdays and weekends differ less than usual.

This result might have been expected based on the conditions that characterize high ozone-forming potential. Studies throughout the world show that low dispersion and intense sunlight are required to reach relatively high ozone concentrations. Low dispersion is characterized by light winds combined with temperature inversions at low altitudes that trap pollutants near the surface. Intense sunlight drives the photochemical reactions that produce ozone in the lower troposphere. When intense sunlight combines with low dispersion, high surface temperatures are the typical result. High temperatures increase the rates of ozone-forming reactions that do not involve photolysis and can increase the emission rates of some ozone precursors.

Furthermore, the highest ozone concentrations measured at the surface often occur when two or more days in succession have low dispersion and intense sunlight. Under these conditions, pollutants tend to accumulate in the air and carry over from one day to the next. Days with these characteristics are likely to have an abundant supply of ozone from carryover. Some researchers conclude that carryover can contribute significantly to ozone measured at the surface the following day.^{13,14} If ozone from the day before routinely contributes to surface ozone measurements, the ozone from carryover should increase during episodes with high ozone-forming potential.

Ozone carryover on weekends may routinely exceed the scavenging potential of relatively scarce NO emissions. When large amounts of ozone and other materials accumulate under episode conditions, could they cause weekdays to behave more like weekends thereby decreasing the weekend effect? That would be the case if the available ozone starts to exceed the scavenging potential of the higher NO emissions on weekdays.

Since carryover may contribute a high proportion of the ozone measured at the surface on weekends and on weekdays during high-ozone episodes, what are the photochemical conditions under which these ozone molecules are generated?

Ozone Carryover Aloft and the Ozone Weekend Effect

Surface ozone data show clearly that little ozone can persist at the surface from one day to the next at almost all locations in California's urbanized areas. Simultaneously, however, high concentrations of ozone and ozone precursors can carry over above the surface. Ozone-generating processes that contribute to surface ozone measurements occur routinely in the atmosphere between 100 and 1500 meters above ground level ("aloft"). These processes can generate large amounts of ozone during daylight hours. Hour by hour, some of the ozone generated aloft is carried down to the surface by convection or by turbulent mixing where it is measured on the same day. At the end of the day, a large reservoir of ozone and ozone precursors is often sequestered aloft overnight to contribute to ozone measurements and to fresh ozone generation the following day.

The physical processes that govern vertical mixing by convection and turbulence are well known. The processes that form an overnight reservoir aloft may be less familiar. As surface temperatures increase following daybreak, convection takes place. The warm surface air rises (cooling as it does so) until it meets air of a similar temperature. The layer of mixed air at the surface thereby deepens and emissions from the surface are carried upward to mix with the air aloft. Surface temperatures typically reach their maximum and begin to cool sometime in the middle to late afternoon. When this happens, vertical convection breaks down, the air stops mixing, and a large reservoir of ozone and precursors becomes stranded in the air aloft. Overnight, radiant cooling at the surface typically forms a surface-based inversion that further isolates the reservoir aloft from emissions at the surface. Ozone near the surface is almost entirely scavenged by NO emissions or destroyed by contact with materials, leading to the low overnight ozone measurements at the surface. Concentrations of ozone and ozone precursors aloft, however, can remain very high over night.

Under what conditions is ozone generated aloft? Data characterizing conditions at the surface are plentiful, but data characterizing conditions aloft are scarce. Measurements of conditions aloft are usually limited to intensive sampling days during special studies of regional ozone. These studies may use aircraft, balloons, remote-sensing instruments or other techniques to measure conditions aloft. The main purpose of these intensive studies is to characterize the conditions throughout a modeling domain to support simulations of the ozone-forming system. Therefore, the data are limited in their ability to illuminate the reasons for the ozone weekend effect.

Despite their limitations, the available measurements aloft reveal that large amounts of ozone are generated and persist in the air aloft. Furthermore, the NO_x concentration (or total reactive nitrogen, NO_y) decreases more quickly with altitude than does the concentration of total ROG species, especially when ROG reaction products are properly included. As a result compared to surface conditions, NO_x concentrations are usually much lower, ROG/NO_x ratios are substantially higher, ROG reaction products are more prevalent making the ROG mix more active, and NO is virtually absent. For these reasons among others, the ozone-forming system aloft appears to be quite different from that indicated by surface data. In many ways, the photochemical conditions aloft appear to be similar to conditions rather far downwind. That is, the ozone-forming system aloft tends to look more NO_x-limited than the measurements at the surface would indicate.

Most research on the ozone weekend effect relies perforce on analyses of data collected by surface-based monitors and assumes these data represent the conditions under which ozone aloft is formed. Unfortunately, this assumption is not warranted and it may derail one's train of thought. In particular, high ozone at the surface on Sunday does not imply high carryover of ozone and ozone precursors aloft from Sunday to Monday. Similarly, relatively low ozone at the surface on Friday/Saturday does not imply relatively low carryover of ozone and ozone precursors aloft from these days to Sunday. There is every reason to assume, instead, that the loading of the atmosphere aloft at the end of the day reflects the emissions rates for that day (plus a portion from preceding days). Despite the surface data, there is likely to be greater carryover aloft from Friday to Saturday and from Saturday to Sunday than from Sunday to Monday. Empirical data that demonstrate or refute this assertion are not now available. Nevertheless, some analyses are consistent with it. For example, Table 5 shows the mean daily maximum for ozone from May through October in the SoCAB from 1980 through 1998 was lowest on Monday more often than on any other day of the week.

If carryover aloft plays a major role in the ozone weekend effect, some vital questions must be answered. Would regulatory NO_x reductions decrease the amount of ozone generated or carried over aloft? Since weekends may well be affected more than weekdays by ozone from aloft (less scavenging on weekends), would weekend ozone respond favorably to regulatory NO_x reductions? Since weekend days increasingly determine the attainment status of California's major air basins, are regulatory NO_x reductions needed to bring these areas into attainment?

Field studies, smog chamber experiments, and modeling exercises could all help answer these questions. Specially designed field studies could gather the data needed to describe the conditions aloft and how these change from weekdays to weekends. Field studies might even reveal the degree to which ozone generated aloft or carried over from the previous day contributes to surface ozone measurements. Smog chamber studies could start with the conditions aloft and explore the system's response to emission reductions. Alternatively, state-of-the-art simulation models could be used to investigate these relationships.

Unfortunately, all three approaches face significant hurdles. Field studies are complex, expensive, and typically require years to design, fund, and execute. Smog chamber studies may be unable to work effectively with the low concentrations of NO_x that characterize the ozone-forming system aloft. Simulation models, in their turn, have limitations discussed in the next section.

Simulation Models and the Ozone Weekend Effect

Photochemical simulation models face at least three obstacles that presently limit their ability to quantify the cause or causes of the ozone weekend effect.

First, little attention has been given to the ability of these models to generate ozone aloft, that is, between 100 and 1500 meters above the surface. Understandably, most performance evaluations for models focus on the realism of the simulated ozone concentrations at the surface to which people may be exposed. Whether pollutants aloft are contributing properly to these surface concentrations has rarely been considered.

Some researchers who have examined the concentrations aloft report substantially less ozone than measured in the field during the modeled episodes. Models might produce too little ozone aloft for various reasons; a partial list includes wind field uncertainties, incomplete emissions inventories, ongoing development of specific ozone episodes, problematic boundary and/or initial conditions, incomplete chemistry, and invalid extrapolation of chemical mechanisms. A single factor has not emerged as the prime suspect.

One of these issues, the performance of chemical mechanisms under low-NO_x conditions, is particularly pertinent to the issues raised in this paper. The performance of chemical mechanisms under these conditions is under study at this time. Previous research has shown that some mechanisms, including the Carbon Bond IV mechanism, can generate too little ozone when NO_x concentrations fall below 50 to 100 ppb.^{15,16} The more recent SAPRC mechanism may be more suited to low-NO_x conditions; a study commissioned by the ARB is currently evaluating the performance of the SAPRC mechanism in this regard.

The limited observations from special studies almost always indicate that conditions aloft fall in the “low-NO_x” category, where NO_x concentrations are below 50 ppb. In many cases, NO_x is well under 20 ppb, and NO is almost non-existent. No chemical mechanism has been fully validated under such conditions because few (if any) smog chambers have been able to conduct the required experiments. Most smog chamber studies have been carried out at NO_x concentrations of 100 ppb or greater because experiments at lower levels may be strongly affected by uncertainties that are difficult to resolve. Facilities needed for low-NO_x experiments have only been available in recent years, and more are now under construction.

Models that fail to generate realistic ozone concentrations aloft, for whatever reason, will have difficulty quantifying the contribution of ozone aloft to ozone measured at the surface on weekdays or on weekends. Whether ozone aloft is freshly generated or carried over from the previous day, the earlier discussion noted that the ozone aloft is often created under low-NO_x and/or NO_x-limited conditions. Models that generate too little ozone aloft may routinely understate the ozone-reducing benefits that should be attributed to regulatory NO_x reductions.

Weekend emission inventories and weekend episodes are still being developed. Though much progress has been made, comprehensive emission inventories for weekend days in California are only now becoming available. Similarly, weekend episodes are still rather limited. While weekend episodes were a goal of the 1997 Southern California Ozone

Study, few simulations have been carried out on the most promising of these episodes, and results have not been fully validated.

CONCLUSIONS

Three questions were posed in the introduction.

1. When ozone molecules are detected at a surface monitor, where, when, and under what conditions were they generated?
2. On weekdays versus weekends, do ozone molecules detected at surface monitors represent different places, times, and conditions in different proportions?
3. How do the answers to these questions relate to regulatory reductions of ROG and NO_x emissions?

The tools and data needed to supply complete and validated answers to these questions are not yet available. Nevertheless, the analyses in this paper provide a coherent set of plausible, perhaps probable, answers. These answers indicate that the ozone weekend effect does not invalidate regulatory NO_x reductions as an effective ozone abatement strategy. Moreover, they lead to the conclusion that substantive NO_x reductions may be needed to improve the rate of progress toward attainment of ozone standards on weekend days in California's major air basins. The following synopsis presents the essential points that lead to this conclusion.

Ozone molecules detected by surface monitors are generated in various locations under various conditions. Two key locations are "near the surface" and "aloft." Conditions aloft, between 100 and 1500 meters above ground level, have much in common with conditions "downwind." In particular, these conditions include low NO_x (commonly < 20 ppb) and high ROG/NO_x ratios, with NO virtually absent. Ozone formation under these conditions is more NO_x-limited than surface measurements would indicate. Surface data cannot be assumed to represent conditions aloft.

Large reservoirs of ozone and ozone precursors can accumulate and carryover from one day to the next. This phenomenon is especially important when dispersion is low and solar intensity is high, the very conditions that lead to high ozone episodes. During such episodes, a large proportion of ozone measured at the surface is likely to have been formed aloft under conditions that appear to be rather NO_x-limited. That is, lower NO_x would reduce the amount of ozone formed.

Three different types of data indicate that a significant portion (perhaps, the major share) of the ozone weekend effect may be due to ozone scavenging very near ground level by high NO emissions on weekdays. When NO emissions decrease on weekends, the local ozone suppression due to scavenging decreases and weekend ozone measurements at the surface increase.

Long-term ozone trends indicate that these observations and conjectures may explain a great deal of the ozone weekend effect. Thirty years in which the rate of ROG reductions

has exceeded the rate of NO_x reductions has caused greater ozone reductions on weekdays than on weekends. Weekends have been left behind to such an extent that weekend days now play the largest role in determining the attainment status of major air basins in California. In the air basins that have been carefully studied, the ozone weekend effect is relatively small but may be increasing at the downwind receptor sites that determine the attainment status of each air basin.

There is every reason to anticipate that a continuing emphasis on ROG emission reductions will further widen the gap between weekdays and weekends as weekends improve at a slower rate. To accelerate the rate of improvement on weekends, NO_x-reducing regulations may be needed.

DISCLAIMER

The statements and conclusions in this paper are those of the author and not necessarily those of the California Air Resources Board. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products.

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Table 1. Annual average ROG and NO_x emissions inventory* (tons per day) for 1980 and 2000 in four regions of California.

Region	Pollutant	Year		Percent Decrease
		1980	2000	
South Coast Air Basin	ROG	2218	1029	54 %
	NO _x	1743	1131	35 %
Bay Area Air Basin	ROG	1333	552	59 %
	NO _x	966	636	34 %
Sacramento Metro AQMD	ROG	189	97	49 %
	NO _x	133	109	18 %
San Joaquin Valley Air Basin	ROG	1032	477	54 %
	NO _x	775	577	26 %

* From ARB database supporting emissions projections for the 2002 Almanac of Emissions and Air Quality, California Air Resources Board, Planning and Technical Support Division, Sacramento, CA.

Table 2. Rates of progress reducing ozone concentrations in the South Coast Air Basin from 1980 – 1998 based on the average of the 2nd through 11th highest values for daily maximum ozone by day of week.

Sub-Region	Sites Used	Weekdays*	Weekends*
All sites	17	Down 46 %	Down 33 %
Southwest L.A. County	4	Down 46 %	Down 34 %
San Gabriel Valley	3	Down 55 %	Down 36 %
San Fernando Valley	2	Down 49 %	Down 43 %
Orange County	3	Down 43 %	Down 26 %
San Bernardino/Riverside	5	Down 42 %	Down 31 %

* Difference between the 1996/98 and 1980/82 values expressed as percent of the 1980/82 baseline. Weekday values represent Monday through Friday.

Table 3. Comparison of percent change in ozone from Friday to Sunday at Urbanized versus Suburban/Rural sites in four regions of California (data for May-October 1998-2000).

Region	Average Change in Ozone – Friday to Sunday			
	Urbanized Sites		Suburban/Rural Sites	
	Sites	Average	Sites	Average
South Coast Air Basin	12	29.3%	7	19.0%
San Francisco Bay Area Air Basin	15	26.1%	7	20.7%
Sacramento Metropolitan Area	3	10.5%	12	4.8%
San Joaquin Valley Air Basin	13	8.6%	6	4.4%

Table 4. AIRS ID numbers for sites identified as Urban or Suburban/Rural in four regions of California.

Region	Urban	Suburban/Rural
South Coast Air Basin	060590001 060370002 060371002 060370016 060595001 060371103 060371301 060372005 060371601 060371701 060371201 060711004	060710005 060712002 060659001 060714003 060658001 060719004 060376002
San Francisco Bay Area Air Basin	060130002 060011001 060012001 060851001 060851002 060010005 060133001 060811001 060850004 060852005 060010006 060131003 060410001 060970003 060950004	060131002 060950002 060850002 060010007 060010003 060550003 060852006
Sacramento Metropolitan Area	060670002 060670006 060670010	060610002 060170020 060670012 060170010 060613001 060610006 060675003
San Joaquin Valley Air Basin	060290014 060290010 060195001 060190008 060190007 060190242 060990005 060990010 060290232 060190010 060770009 060771002 061072002	060295001 060290007 060311004 060290008 060194001 060773003

Table 5. Frequency (site-years) with which different days of the week recorded the lowest mean of daily maximum ozone measurements during the May to October ozone season.

Years	Site-years with the lowest mean maximum ozone by day-of-week						
	Sun.	Mon.	Tue.	Wed.	Thu.	Fri.	Sat.
1980 – 1998	61	212	68	89	103	65	9
1980 – 1984	33	61	18	14	37	9	3
1985 – 1990	23	44	19	24	26	18	6
1994 – 1998	1	45	25	37	24	12	0

Table 6. Surface ozone for weekdays and weekends expressed as percent of ozone at 100 m above ground level, based on ozonesondes at 2 p.m. during the 1997 South Coast Ozone Study.

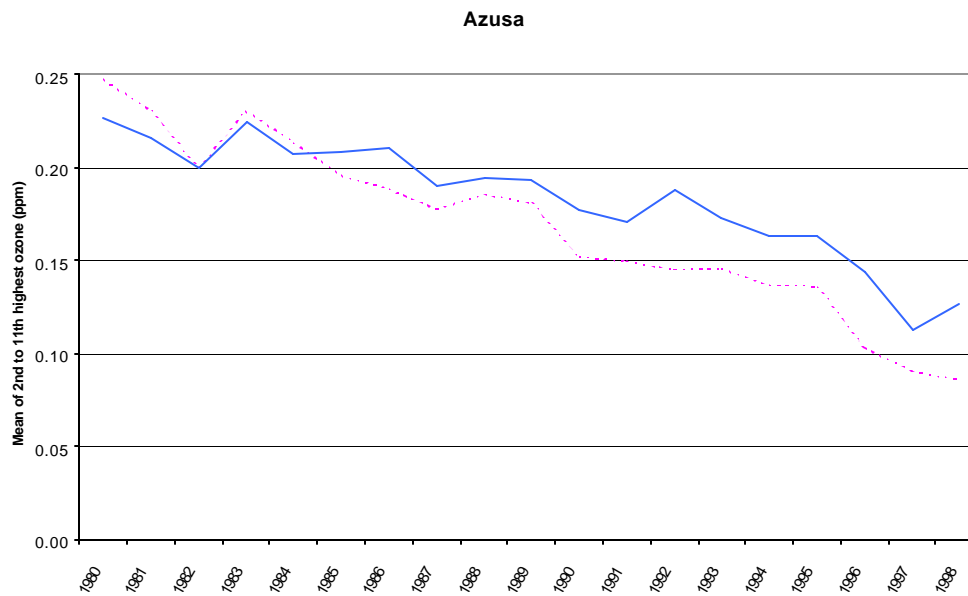
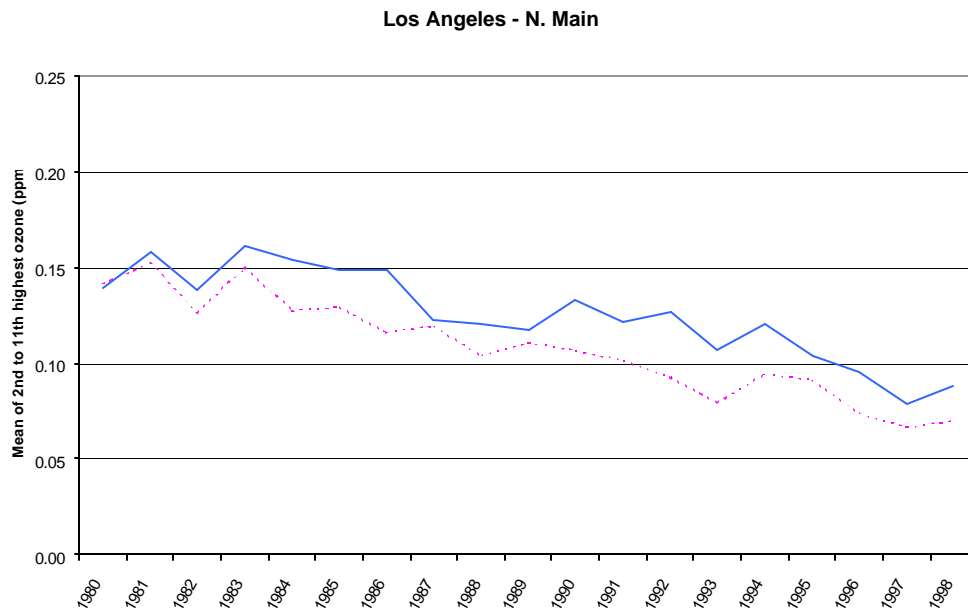
Location	Weekdays	Weekends
Anaheim	15% (8) [*]	13% (4)
Los Angeles	9% (7)	8% (4)
Northridge	17% (8)	13% (4)
Pomona	23% (9)	17% (4)
Riverside	20% (6)	9% (4)

^{*} The number of ozonesondes available is given in parentheses.

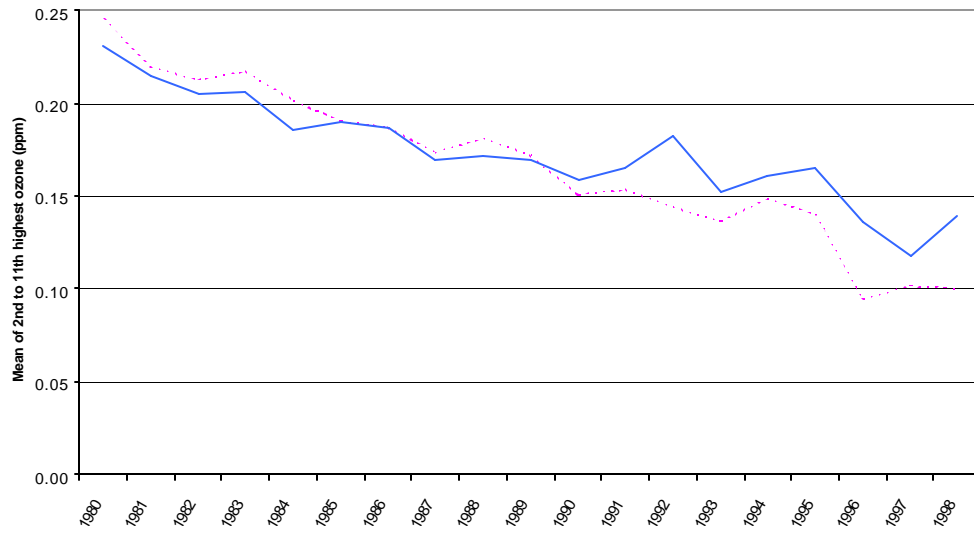
Table 7. Comparison of total oxidant (ozone plus nitrogen dioxide) at locations in the South Coast Air Basin based on data for 1998 – 2000.

Location	Total Oxidant (ppb)		Difference (% of WD)
	WD	WE	
Hawthorne	69	71	2.5%
Pasadena	98	103	4.4%
Pico Rivera	97	102	6.1%
San Bernardino	107	116	8.5%
La Habra	85	90	6.9%
Fontana	105	114	8.6%
Reseda	78	79	0.9%
N. Long Beach	76	79	3.6%
Azusa	110	118	7.2%
Upland	109	119	8.7%
Burbank	104	105	0.6%
West L.A	67	69	2.9%
Lynwood	75	78	4.3%
Riverside	94	100	7.2%
Anaheim	78	83	6.7%
Glendora	109	117	7.6%
Santa Clarita	92	94	1.6%
Pomona	106	114	8.1%
Los Angeles - N. Main	91	94	3.0%
Costa Mesa	63	65	3.7%
Lake Elsinore	88	91	3.5%
Banning	95	95	-0.8%
Basin Average			4.8%

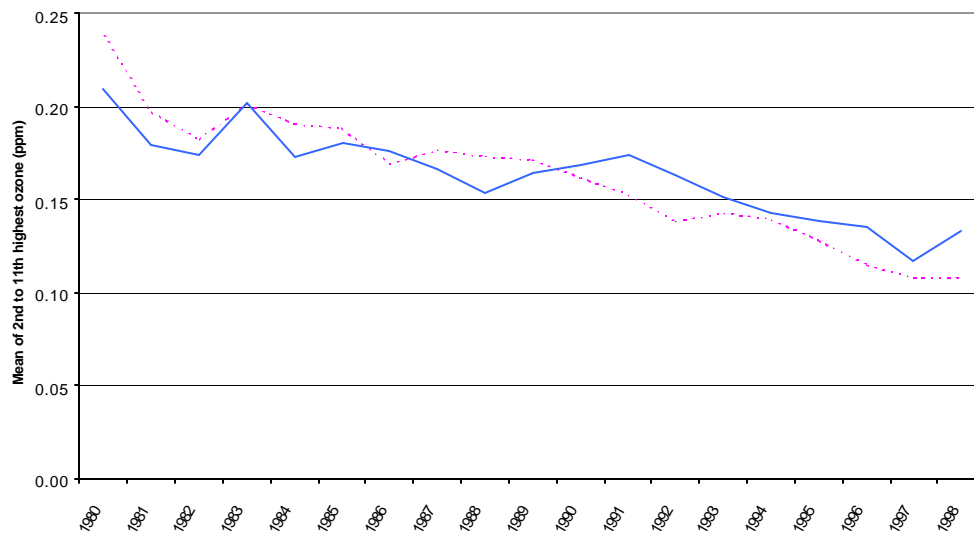
Figure 1. Ozone trends from 1980 to 1998 on weekdays and weekends at selected sites in the South Coast Air Basin.



Upland



Riverside-Rubidoux



Lake Gregory

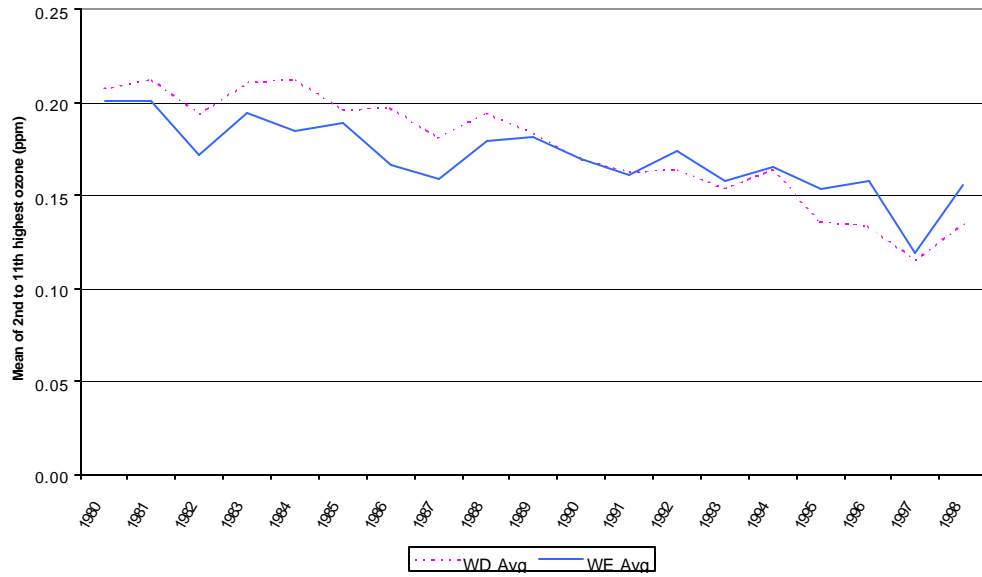


Figure 2. Activity of light-duty vehicles by day-of-week – composite of 11 Weigh-in-Motion stations in the South Coast Air Basin of California.

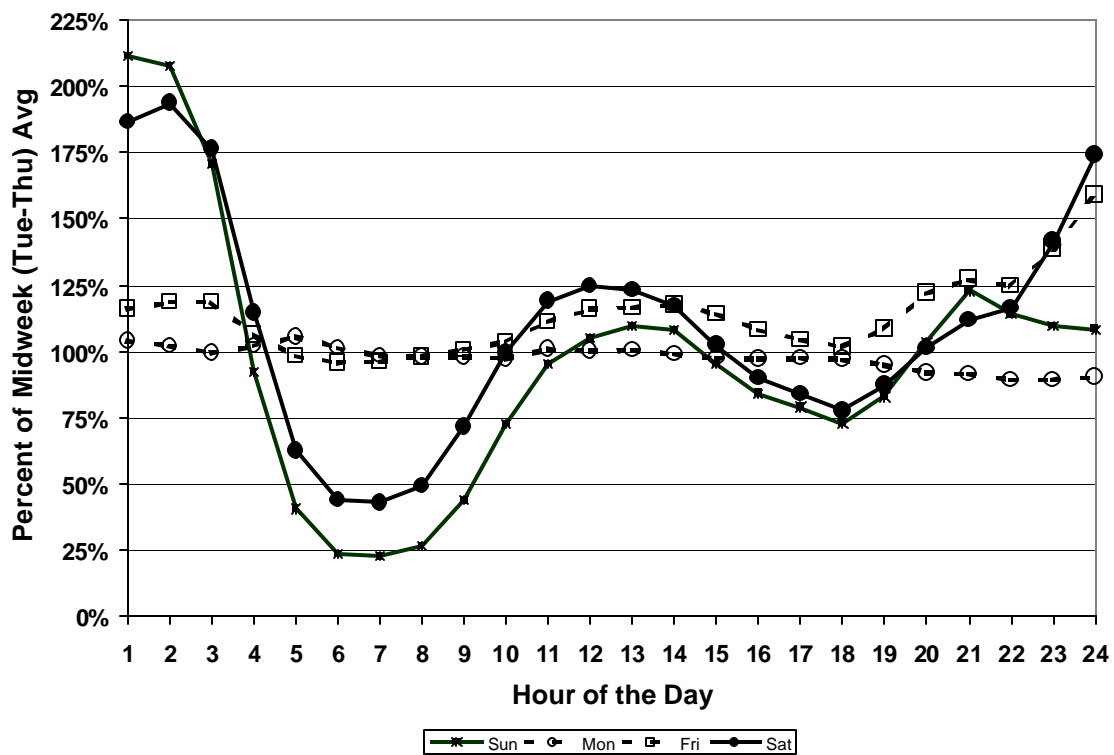
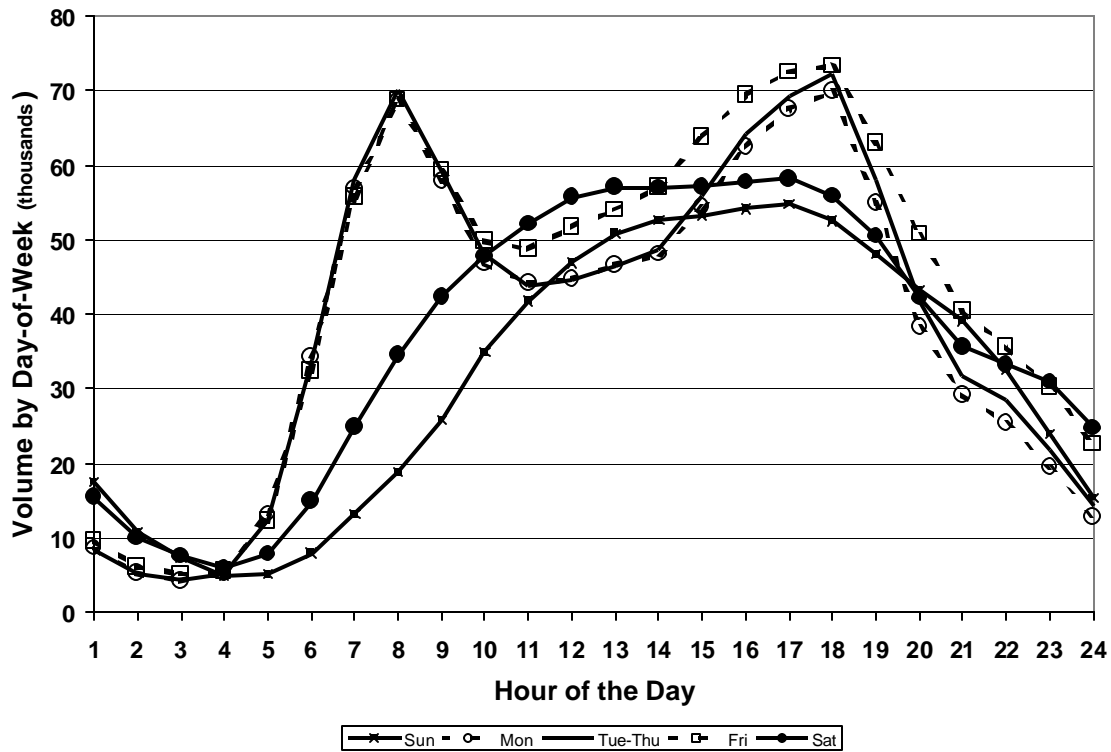


Figure 3. Activity of heavy-duty vehicles by day-of-week – composite of 11 Weigh-in-Motion stations in the South Coast Air Basin of California.

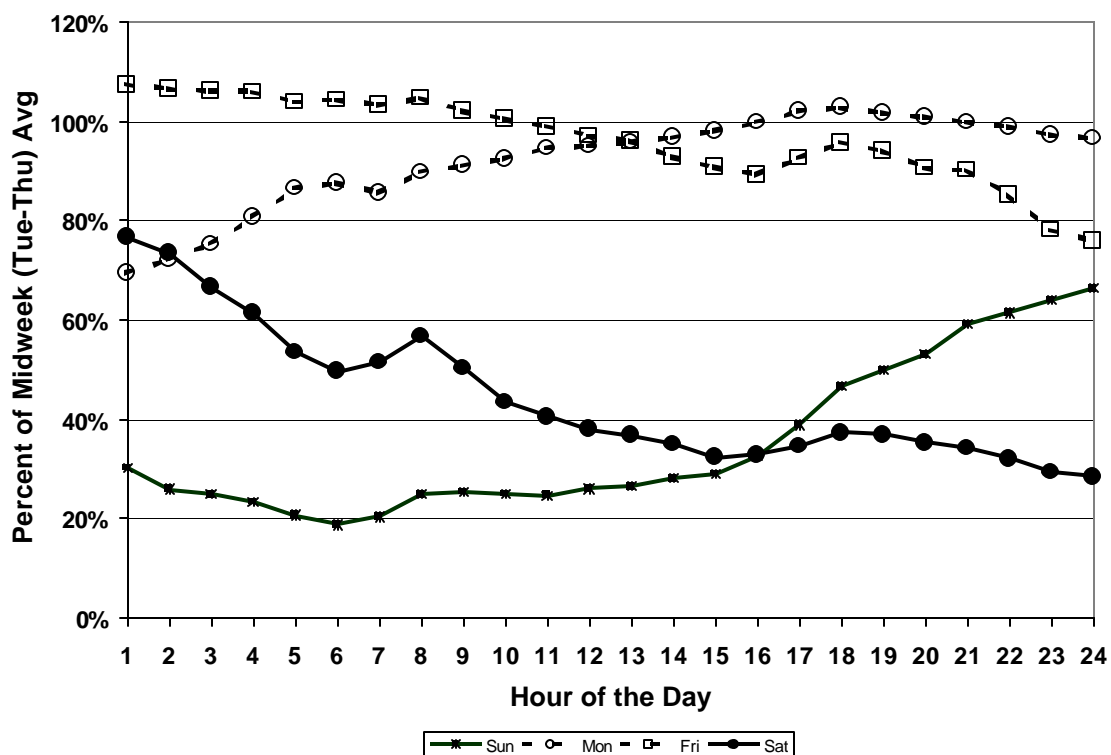
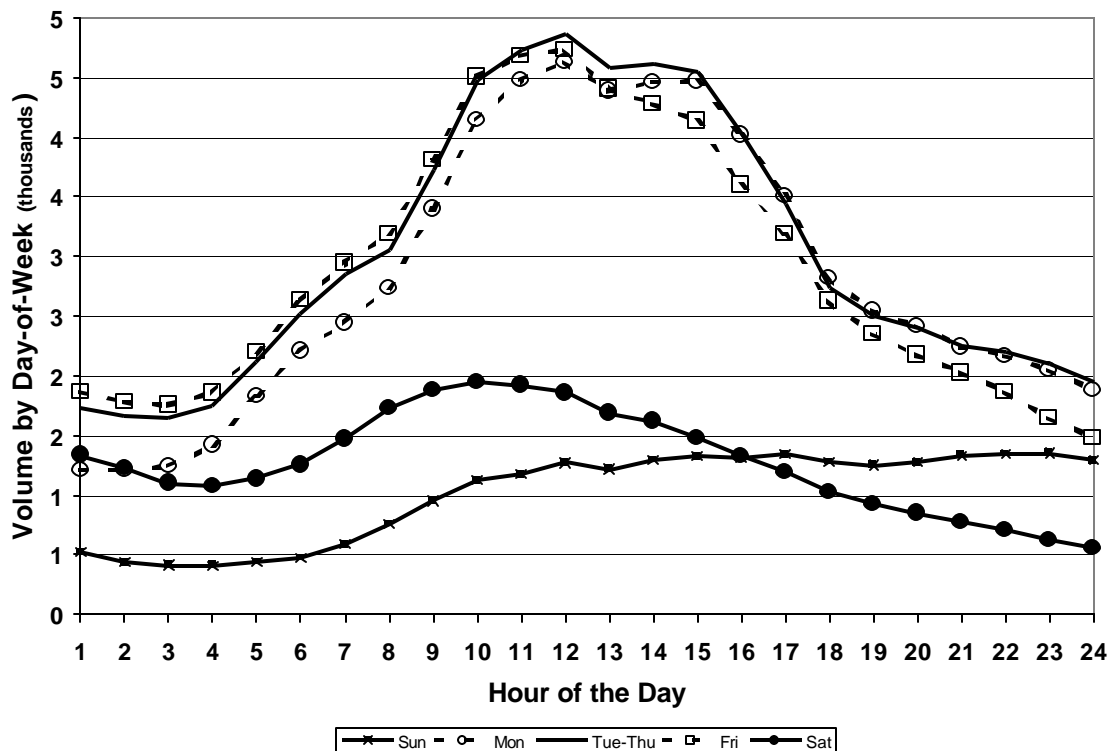


Figure 4. Hourly values of NO_x by day-of-week expressed as a percent of midweek (Tue-Thu) value; composite of 11 sub-regions of the South Coast Air Basin

